Supporting Information

Transformation of Extra-large Pore Germanosilicate CIT-13 Molecular Sieve into Extra-large Pore CIT-5 Molecular Sieve

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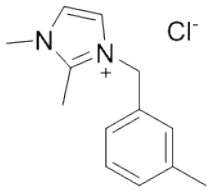
Synthesis of Organic Structure Directing Agents

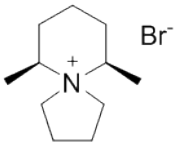
Materials

1,2-Dimethylimidazole (98%, Alfa Aesar), 3-methylbenzyl chloride (98%, Sigma-Aldrich), 1,4-dibromobutane (99%, Sigma-Aldrich), cis-2,6-dimethylpiperidine (99%, TCI America), N-methylpyrrolidine (97%, Sigma-Aldrich), 1,5-dibromopentane (97%, Sigma-Aldrich), N,N,N′,N′-tetramethylhexamethylenediamine (99%, Sigma-Aldrich), (-)-sparteine (99%, Aldrich), and methyl iodide (99%, with Cu as stabilizer, Sigma-Aldrich) were used as received without further purification.

Organic Syntheses

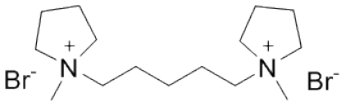


1,2-dimethyl-3-(3-methylbenzyl)imidazolium chloride (12DM33MBI$^+$Cl$^-$) was prepared from the S_N2 reaction between 1,2-dimethylimidazole and 3-methylbenzyl chloride.[1] 1,2-Dimethylimidazole (19.2 g, 200 mmol) was dissolved in 500 ml of toluene. While stirring, 3-methylbenzyl chloride (28.1 g, 200 mmol) was added dropwise. The reaction mixture is heated up to 105 °C and stirred for 72 hours. As the reaction proceeds, bright-yellowish powder product that is insoluble in toluene started to appear. The solid was collected by filtration, and washed with diethyl ether (~ 1 liter) and dried in a vacuum at room temperature.

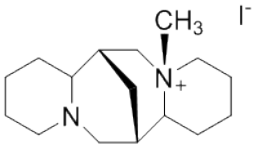


(6R,10S)-6,10-dimethyl-5-azaspiro[4.5]decanium bromide (DMASD$^+$Br$^-$) was prepared from the nucleophilic annulation reaction between cis-2,6-dimethylpiperidine and 1,4-dibromobutane.[2-3] 160 ml of 1 M NaOH aqueous solution was mixed with 32.3 g (150 mmol) of 1,4-dibromobutane by stirring vigorously. The mixture was heated up to the reflux temperature, and 17.0 g (150 mmol) of cis-2,6-dimethylpiperidine was added dropwise to the mixture. The reaction was conducted under reflux overnight. And then, the mixture was cooled down in a dry-ice bath and 50% NaOH aqueous solution was added until a light brownish oil-like phase appeared. This second phase was frozen by extended cooling. The solid phase was collected by filtration, and extracted with 200 ml of chloroform three times. The collected chloroform phase was dried using an excess amount of anhydrous magnesium sulfate. A clear solution was obtained after filtering out magnesium sulfate. Using a rotary evaporator, excess chloroform was removed, and the product was re-dispersed in a small portion (<100 ml) of chloroform. This dense solution was added

dropwise into vigorously stirred diethyl ether to turn the product into powdery form. The obtained product was collected by filtration, and washed with copious amount of diethyl ether, and dried in a vacuum at room temperature.



1,5-bis-(methylpyrrolidinium)-pentane dibromide ($MPP^{2+}Br_2^-$) was prepared from the S_N2 reaction between N-methylpyrrolidine and 1,5-dibromopentane.[4-5] N-methylpyrrolidine (25.5 g, 300 mmol) was dissolved in 350 ml of acetone, and 23.0 g (100 mmol) of 1,5-dibromopentane was added dropwise while vigorously stirring. The mixture was stirred under reflux for 48 hours, and the product organic salt was collected by filtration. The product was thoroughly washed with acetone and diethyl ether, and dried in a vacuum at room temperature.



N-methylsparteinium iodide ($MSpa^+I^-$) was prepared from the S_N2 reaction between (-)-sparteine and methyl iodide.[6-7] (-)-Sparteine (23.5 g, 100 mmol) was dissolved in 300 ml of chloroform, and cooled in a dry-ice bath. Methyl iodide (19.9 g, 140 mmol) was added dropwise and stirred for a week at room temperature in a dark place. 600 ml of diethyl ether was added, and the solid phase product that appeared as the result of ether addition was separated by filtration. The product was thoroughly washed with extra diethyl ether, and dried in a vacuum at room temperature.

Ion-Exchange and Titration

The quaternary ammonium halide salts obtained from the procedures described above were dissolved in distilled water. The anion ion-exchange was performed using Dowex™ Monosphere™ 550A (OH-form, Dow Chemical) ion-exchange resin. The solutions were stirred overnight with ion-exchange resin (mixing ratio: 3 ml of ion-exchange resin per 1 mmol of organic halide salt). The used resin was removed by filtration, and the solution phase was concentrated using a rotary evaporator. The molarity of quaternary ammonium hydroxide solution was determined by titration using a Mettler Toledo DL22 titrator.

Synthesis of Molecular Sieves

Materials

Tetraethyl orthosilicate (TEOS, 98%, Alfa Aesar), fumed silica (Acros Cab-O-Sil®), Ludox HS-30 colloidal silica (30 wt. % SiO_2 in water, Sigma-Aldrich), germanium (IV) oxide (Strem, 99.999%), hydrogen fluoride (HF, 48% in H_2O, Sigma-Aldrich), ammonium fluoride (98%, Sigma-Aldrich), lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$, 98.5–101.5%, Sigma-Aldrich) were used as received without extra purification steps.

Synthesis Conditions

Ge-CIT-13 (*CTH)

Ge-CIT-13 germanosilicates were prepared using $12DM33MBI^+OH^-$ as the OSDA in fluoride media following the procedure which we reported previously.[1] Specifically, the desired amount of germanium oxide and TEOS were hydrolyzed in a desired amount of $12DM33MBI^+OH^-$ solution in a 23 ml PTFE liner for Parr autoclaves. The mixture was stirred until it became a single transparent phase. Excess ethanol and water were evaporated under an air flow until the gel became viscous. The desired amount of HF solution was added and manually stirred by a clean PTFE rod. (*Caution: appropriate personal protective equipment (PPE) and ventilation are strongly required when dealing with HF solution.*) As a result of HF addition, the mixture turned into white powdery gel. The excess HF and water were evaporated in a fume hood for 1–2 days. Finally, the desired amount of water was added and mixed. The final gel molar composition was $x/(x+1)$ SiO_2 : $1/(x+1)$ GeO_2 : 0.5 $12DM33MBI^+OH^-$: 0.5 HF : 10 H_2O where x is the gel Si/Ge molar ratio. ($3.0 < x < 5.5$) The empirical relation between gel Si/Ge ratios and product Si/Ge ratios is provided in our previous report.[1] The mixture was sealed in a steel autoclave (Parr Instrument) and crystallized in a rotating or static oven at 160 °C for 2 weeks. The resultant product was washed with distilled water and acetone, and dried in a convection oven at 100 °C.

IM-12 (UTL)

IM-12 germanosilicate was synthesized using $DMASD^+OH^-$ as the OSDA following the procedures reported previously.[2-3] Desired amounts of fumed silica and germanium oxide were hydrolyzed in $DMASD^+OH^-$ solution in a 23-mL PTFE liner, and stirred for ca. 24 hours until homogenized. After that, a desired amount of water was added (or evaporated from the gel under an air flow) to make the target gel composition. The final gel molar composition was 0.67 SiO_2 : 0.33 GeO_2 : 0.25 $DMASD^+OH^-$: 30 H_2O. The mixture was sealed in a Parr steel autoclave and crystallized in a rotating oven (70 rpm) at 175 °C for 2 weeks. The resultant IM-12 germanosilicate was rinsed with distilled water and acetone repeatedly, and dried in a convection oven at 100 °C overnight.

ITQ-22 (IWW)

ITQ-22 germanosilicates were synthesized using $MPP^{2+}(OH)_2^-$ as the OSDA following the Corma's original paper.[4] Specifically, desired amounts of TEOS and germanium oxide were hydrolyzed in $MPP^{2+}(OH)_2^-$ solution in a 23-ml Parr PTFE liner by stirring overnight. After that, excess water and ethanol were evaporated under an air flow. The final gel molar composition was 0.67 SiO_2 : 0.33

GeO_2 : 0.25 $MPP^{2+}(OH)_2^-$: 7.0 H_2O. The mixture was sealed in a Parr steel autoclave and crystallized in a rotating oven (70 rpm) at 175 °C for 1 week. The resultant product was washed with distilled water and acetone, and dried in a convection oven at 100 °C.

JLG-18 (ITH)

JLG-18 germanosilicates were synthesized using N,N,N′,N′-tetramethyl-1,6-hexanediamine as the OSDA following the method described by Ren et al.[8] In the desired amount of distilled water, the diamine, TEOS, and germanium oxide were added and homogenized. After that, the desired amount of ammonium fluoride was added and stirred overnight. The final gel molar composition was 0.43 SiO_2 : 0.57 GeO_2 : 7.0 diamine : 1.40 NH_4F : 44 H_2O where x is the gel Si/Ge molar ratio. The mixture was sealed in a steel autoclave (Parr Instrument) and crystallized in a rotating or static oven at 175 °C for 1 week. The resultant product was washed with distilled water and acetone, and dried in a convection oven at 100 °C.

Pure-Silica CIT-5 (CFI)

Pure-silica CIT-5 was synthesized using $MSpa^+OH^-$ as the OSDA in the presence of Li^+ as we described in the previous report.[6] To be specific, desired amounts of lithium hydroxide monohydrate and HS-30 colloidal silica were added to the desired amount of $MSpa^+OH^-$ solution, and the mixture was stirred overnight. The gel molar composition was 1.0 SiO_2 : 0.10 LiOH : 0.24 $MSpa^+OH^-$: 40 H_2O. The resultant translucent gel was charged in a 23-ml PTFE liner and sealed in a Parr autoclave. The crystallization was performed in a static oven at 175 °C for 7 days. The resultant product was washed with distilled water and acetone, and dried in a convection oven at 100 °C.

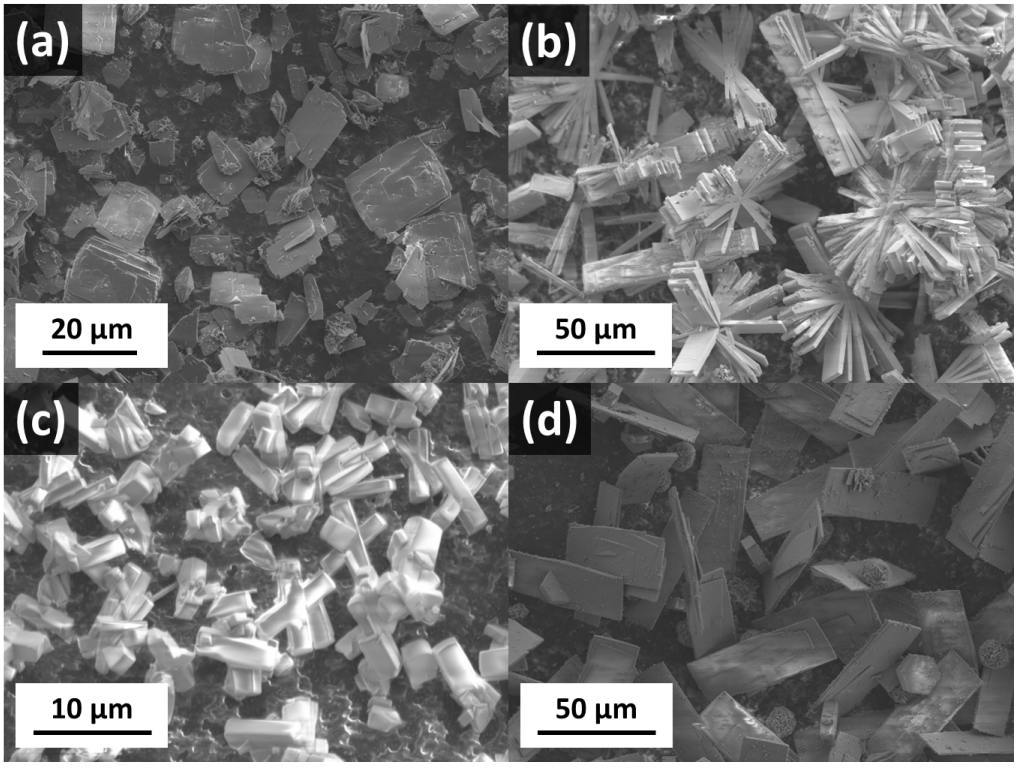


Figure S1. SEM images of germanosilicate and pure-silica molecular sieves shown in this work other than CIT-13-related materials: (a) IM-12 UTL, (b) JLG-18 ITH, (c) ITQ-22 IWW, (d) pure-silica Spa-CIT-5.

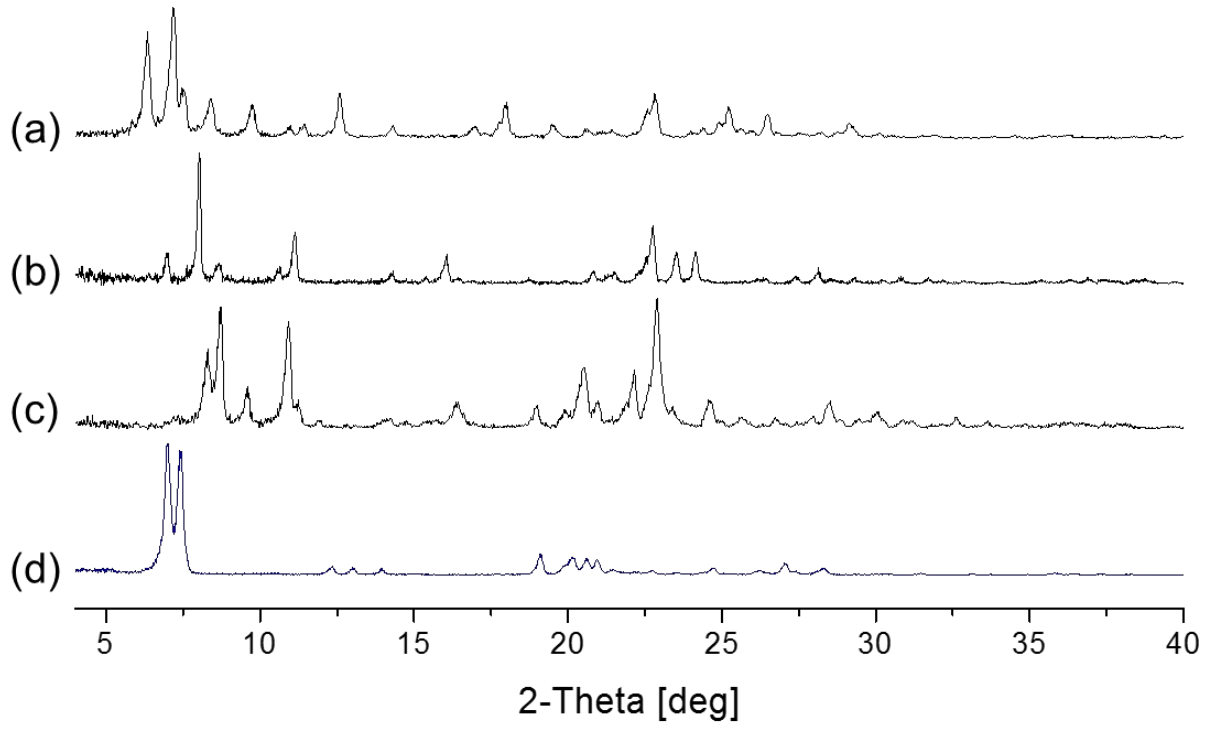


Figure S2. PXRD profiles of as-made molecular sieves prepared to make comparisons with Ge-CIT-13: (a) IM-12 UTL, (b) JLG-18 ITH, (c) ITQ-22 IWW, and (d) pure-silica Spa-CIT-5.

The *CTH-to-CFI transformation

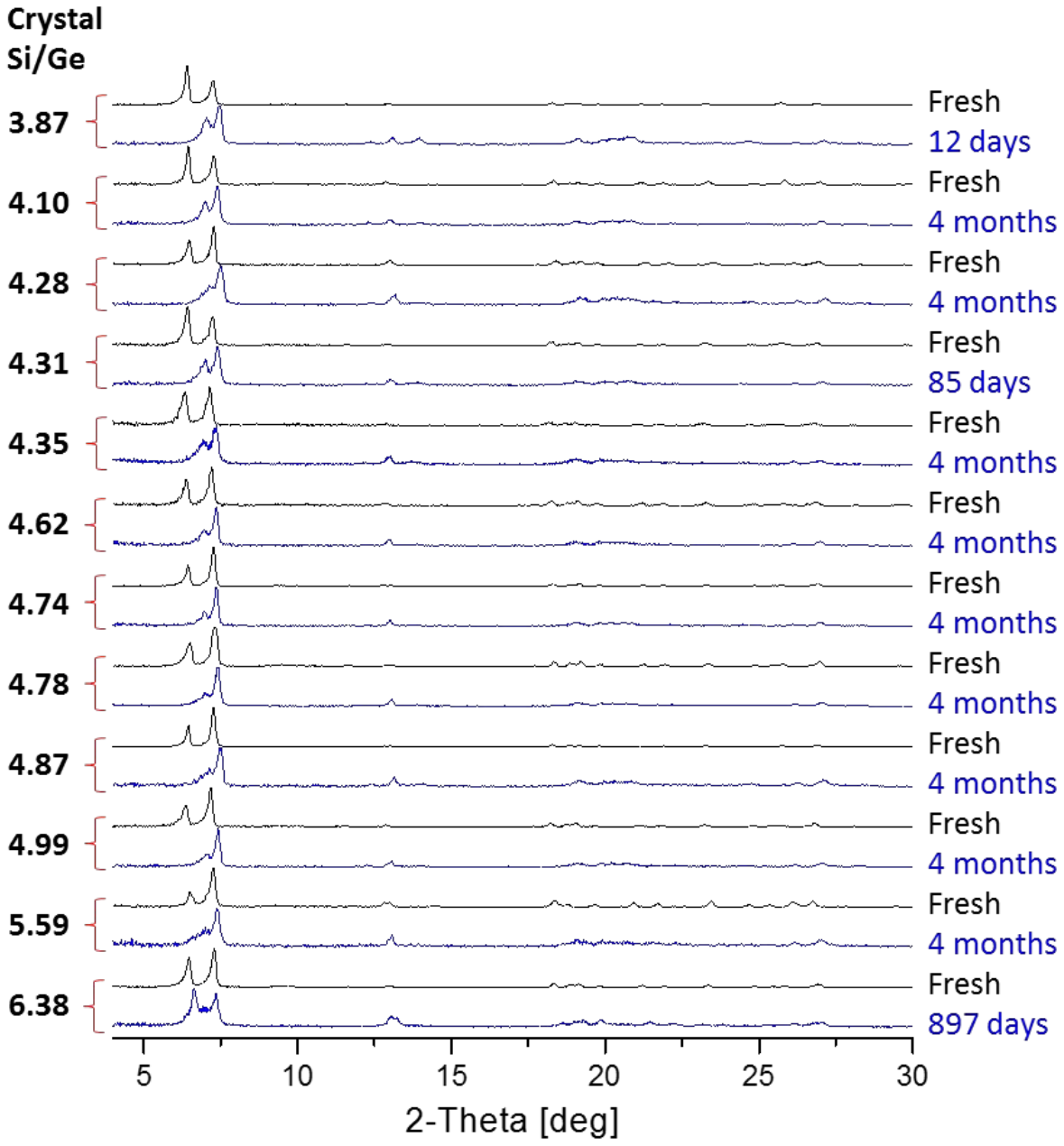


Figure S3. PXRD profiles freshly calcined Ge-CIT-13 samples having various Si/Ge ratios and the same samples after 4 months (unless otherwise noted) of ambient air moisture exposures.

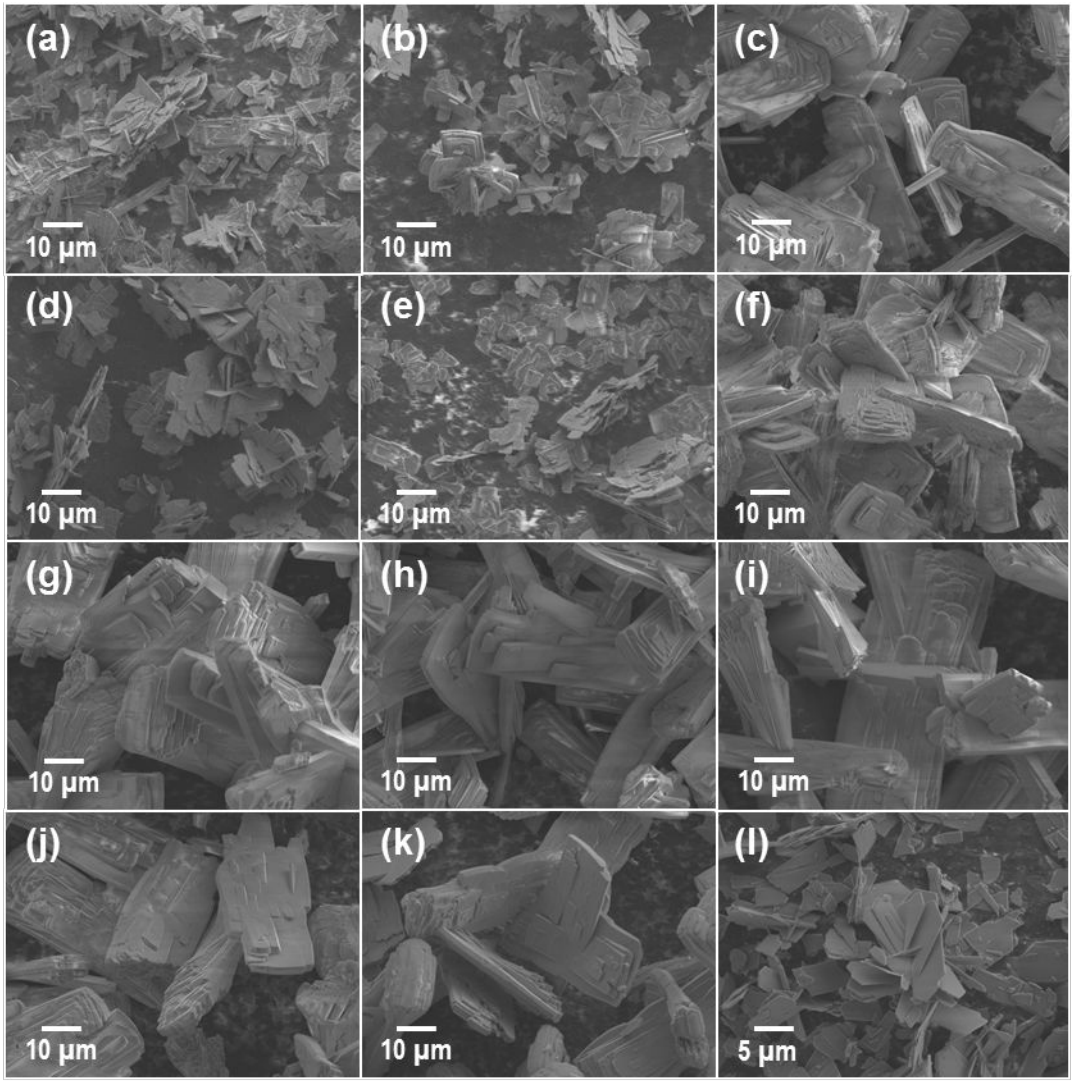


Figure S4. SEM images of as-prepared Ge-CIT-13 samples from various hydrothermal synthesis conditions: (a) Ge-CIT-13[3.87], (b) Ge-CIT-13[4.10], (c) Ge-CIT-13[4.28], (d) Ge-CIT-13[4.31], (e) Ge-CIT-13[4.35], (f) Ge-CIT-13[4.62], (g) Ge-CIT-13[4.74], (h) Ge-CIT-13[4.78], (i) Ge-CIT-13[4.87], (j) Ge-CIT-13[4.99], (k) Ge-CIT-13[5.59], and (l) Ge-CIT-13[6.38].

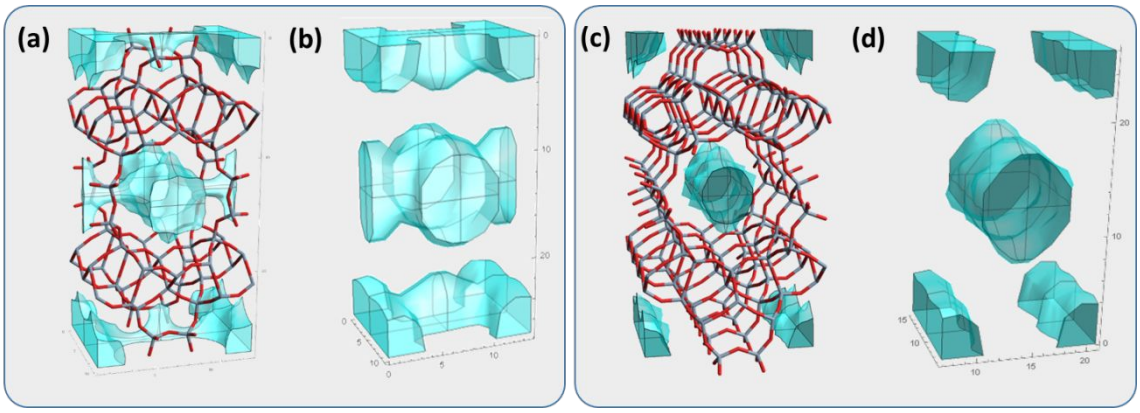


Figure S5. Visualizations of (a) the region accessible to the center of spherical probe argon atom (Ac-PC) and (b) the probe-occupiable volume in a single unit cell of CIT-13 (Ac-PO). Those of (c) the Ac-PC region and (d) the Ac-PO volume in a single unit cell of CIT-5.

Micropore volumes of Ge-CIT-13 and Ge-CIT-5 were theoretically estimated on the basis of the assumptions proposed by Nagy et al., and Ongari et al.[9-10] To be specific, all framework atoms and probe molecules are assumed to be hard spheres. Also, no thermal vibration and complete preservation of crystallographic parameters (e.g., lattice parameters) were assumed.[10] The crystallographic information of CIT-13 and CIT-5 were obtained from the IZA database.[11] The computation was performed using Wolfram Mathematica 10.1 Student Edition and Version 12.0 of the same software. For visualization of frameworks, the Crystallica application developed by Bianca Eifert at Justus Liebig University Giessen was used.

The computation of pore volume was accomplished in three steps. First, the region where the center of probe molecule can access was determined. This region corresponds to the region denoted as "*accessible probe center* (Ac-PC)" by Ongari et al.[10] The following equation was used to determine the surface of the Ac-PC region.[9]

$$d(\vec{\boldsymbol{r}}) = \min\left(\sqrt{\left(\overrightarrow{\boldsymbol{R_i}} - \vec{\boldsymbol{r}}\right)^2}\right) - r_{vdW} - r_{Ar} = 0$$

$\overrightarrow{\boldsymbol{R_i}}$ is the position of the i-th framework atom, and r_{vdW} and r_{Ar} are the van der Waals radius of framework atoms (1.35 Å) and the kinetic radius of argon atom (1.7 Å). The resultant visualizations of the Ac-PC regions of CIT-13 and CIT-5 are shown in Figure S5(a) and (c), respectively.

Second, the region that can be occupied by the probe molecule was determined. From the surface of the obtained Ac-PC region, the second surface that is "dilated" by the radius of probe molecule was determined. This surface is the boundary of the occupiable region that was denoted as "*accessible probe-occupiable* (Ac-PO)" by Ongari et al.[10] The Ac-PO regions of CIT-13 and CIT-5 are illustrated in Figure S5(b) and (d), respectively.

Lastly, the volume of the Ac-PO region within a single unit cell was calculated. For CIT-13 and CIT-5, the occupiable volumes are 1501.16 $Å^3$ (per $T_{64}O_{128}$-*CTH) and 461.376 $Å^3$ (per $T_{32}O_{64}$-CFI), respectively. When the Si/Ge ratio is 4.22, the theoretical micropore volumes are 0.206 cc/g and 0.126 cc/g for Ge-CIT-13 and Ge-CIT-5, respectively. Therefore, the theoretical micropore volume of Ge-CIT-5 corresponds to 61% of that of Ge-CIT-13 (a 39% reduction), as mentioned in the main text.

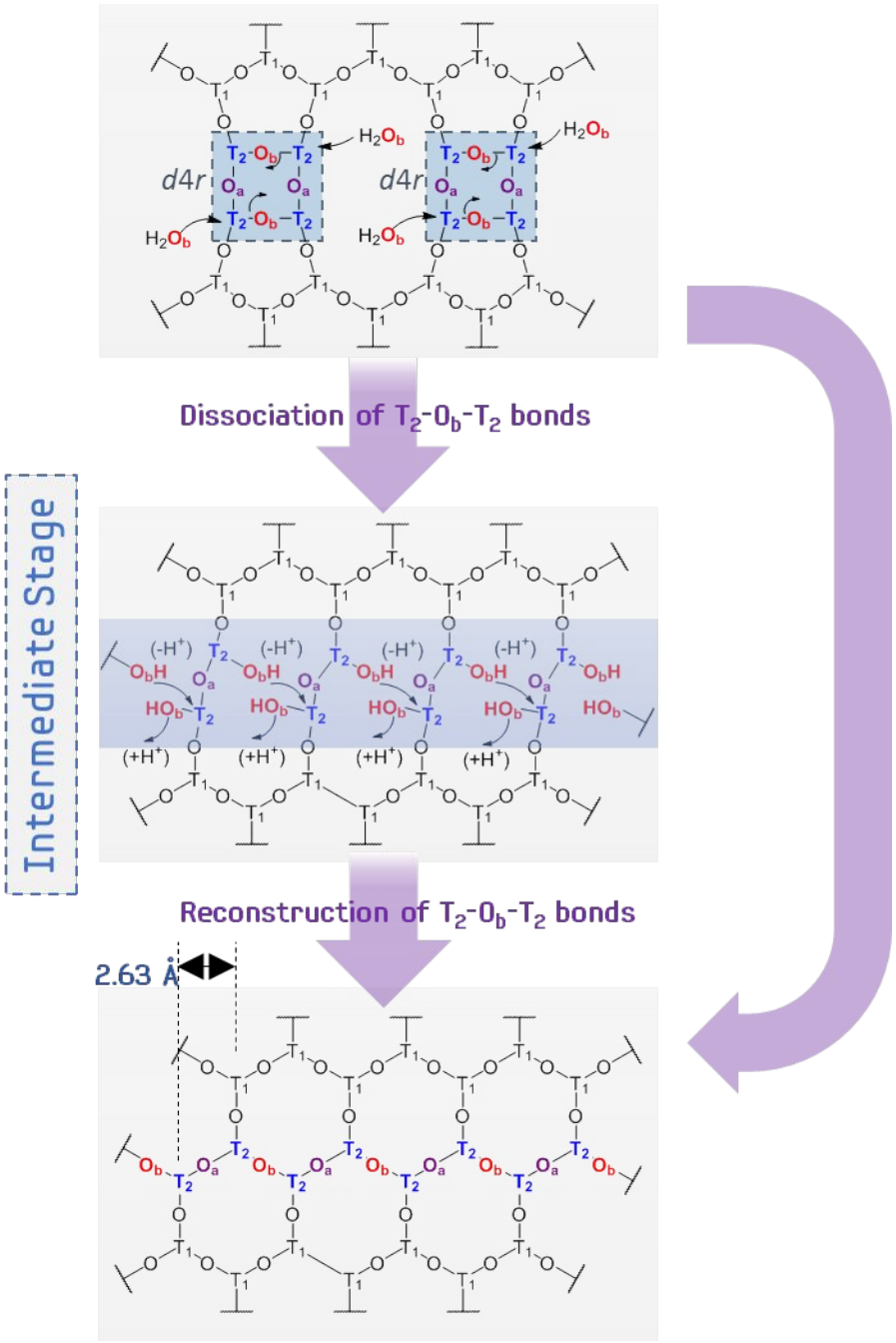


Figure S6. Schematic description of the 'net' transformation from Ge-CIT-13 to Ge-CIT-5, seen along the 10-ring direction. (*cfi*-layer T-atoms and *d4r* T-atoms were denoted as T_1 and T_2, respectively.) The T_2-O_b-T_2 bonds of the d4r units, which are parallel to the 14-ring main channels, must be dissociated and reconstructed to achieve the transformation. Other T-O-T bonds can be hydrolyzed, but must be restored to form the final CFI framework.

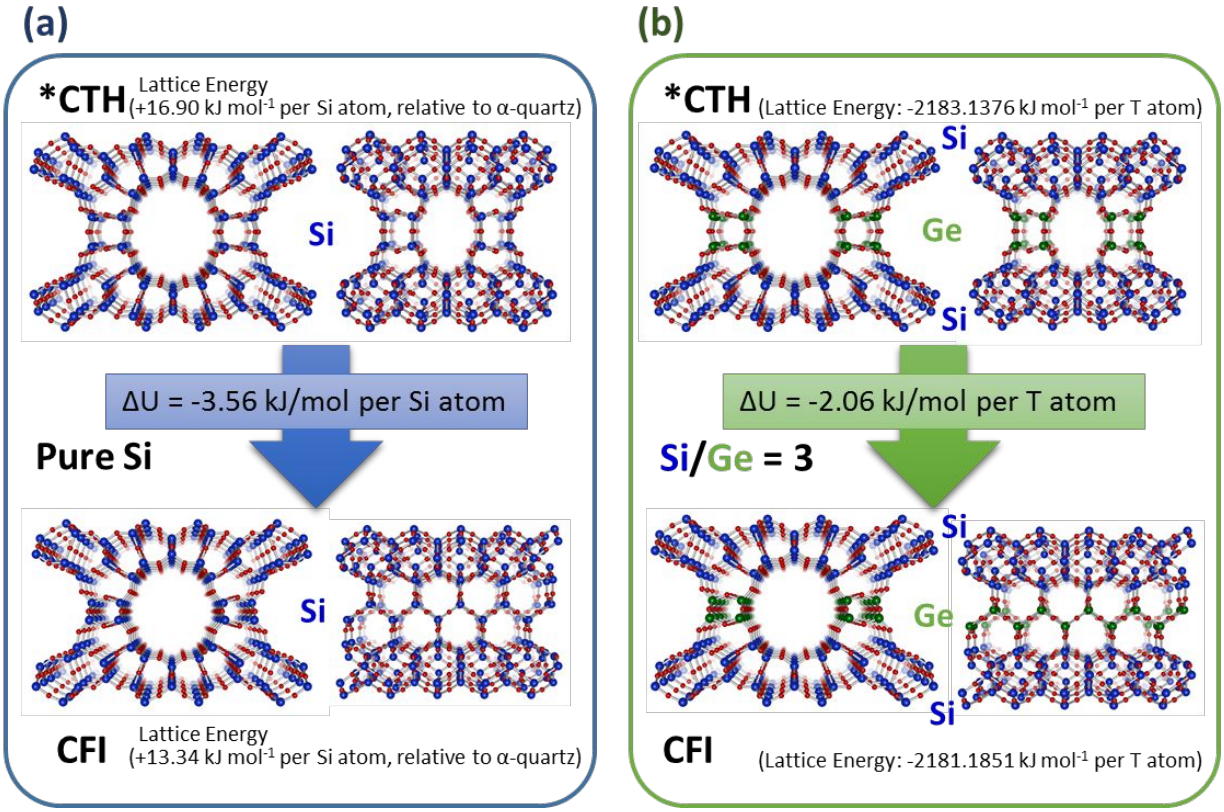


Figure S7. The lattice models used to calculate lattice energies: (a) pure-silica *CTH and CFI, and (b) hypothetical germanosilicate (Si/Ge = 3) crystal models of *CTH and CFI whose *cfi*-layers are exclusively composed of pure silica and whose connecting units—*d4r* and *dzc*— are completely composed of germanium oxide.

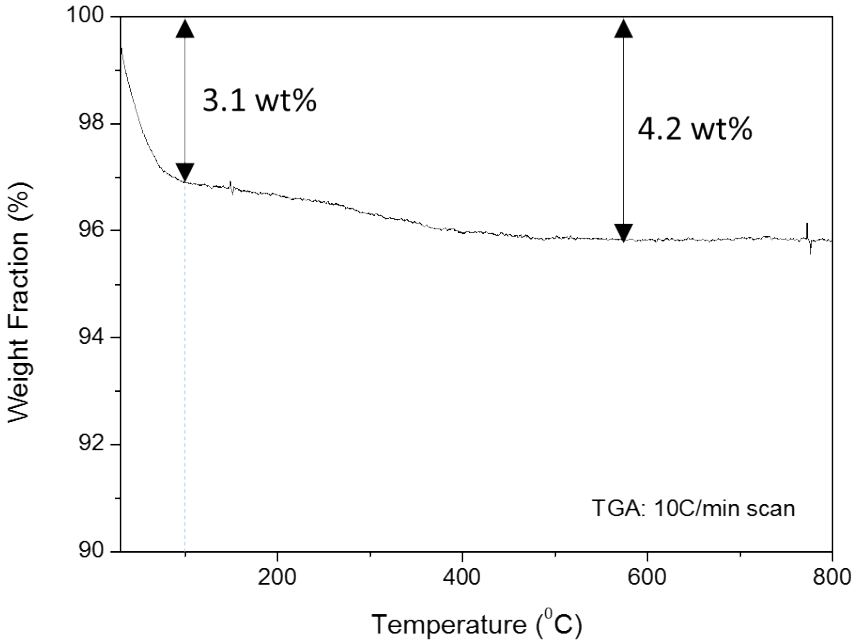


Figure S8. TGA profile of Ge-CIT-13[4.31] which had been exposed to 30 % relative humidity at 25 °C for 4 months. At this point, the PXRD profile indicated that the initial *CTH framework was already collapsed into the CFI framework.

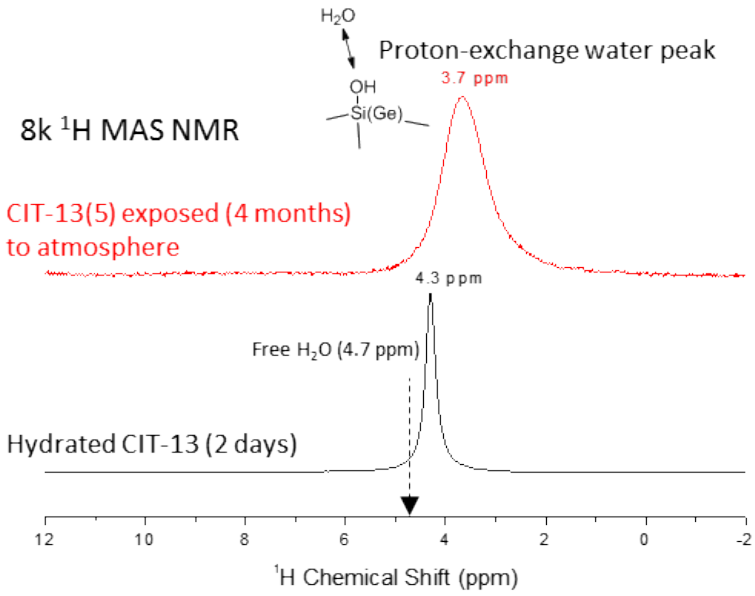


Figure S9. ^{1}H 8 kHz MAS spectra of Ge-CIT-13[4.31] which had been exposed to 30 % relative humidity at 25 °C for 4 months (top, red) and the same Ge-CIT-13 exposed to 100 % saturated humidity at 25 °C for 2 days (bottom, black).

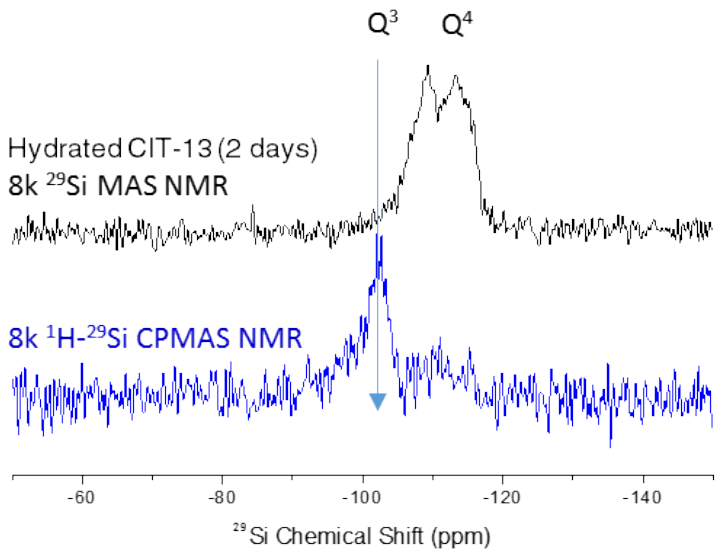


Figure S10. ^{29}Si MAS (top, black) and ^{1}H-^{29}Si CPMAS (bottom, blue) spectra of Ge-CIT-13[4.31] exposed to 100 % saturated humidity at 25 °C for 2 days.

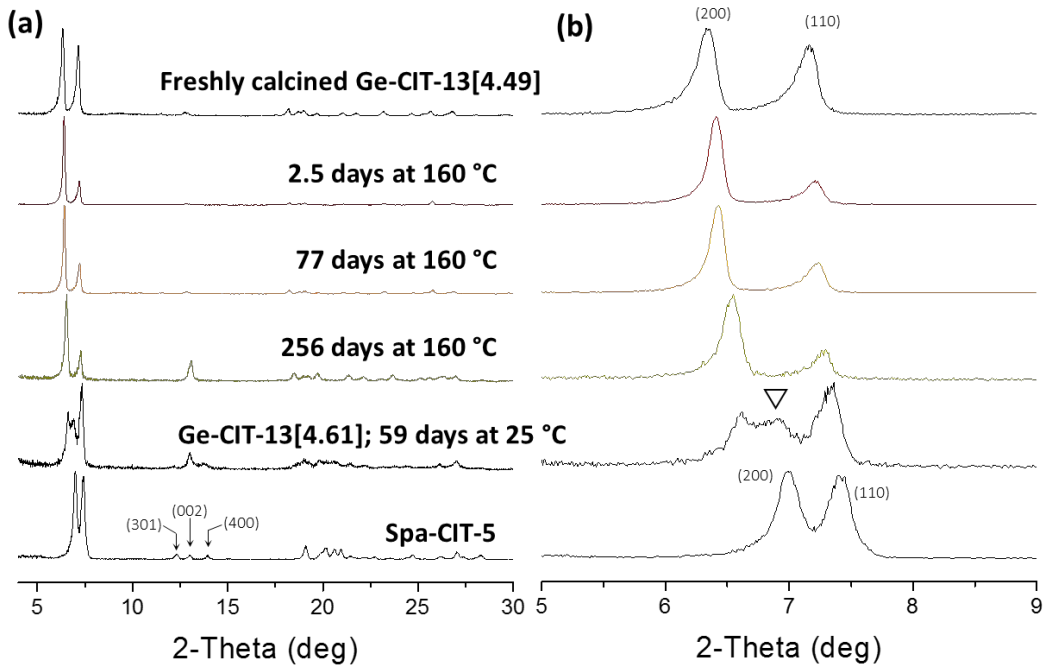


Figure S11. PXRD profiles of calcined Ge-CIT-13[4.49] stored in a 160 °C convection oven supplied with the lab ambient air flow after 2.5, 77, and 256 days. PXRD profiles of Ge-CIT-13[4.61] stored at 25 °C after 59 days under the same humidity and that of the reference Spa-CIT-5 were provided together for comparison: in (a) 4–30° wide angle and

(b) 5–9° zoomed-in regions. (The triangular mark (▽) indicates inhomogeneity of the sample.)

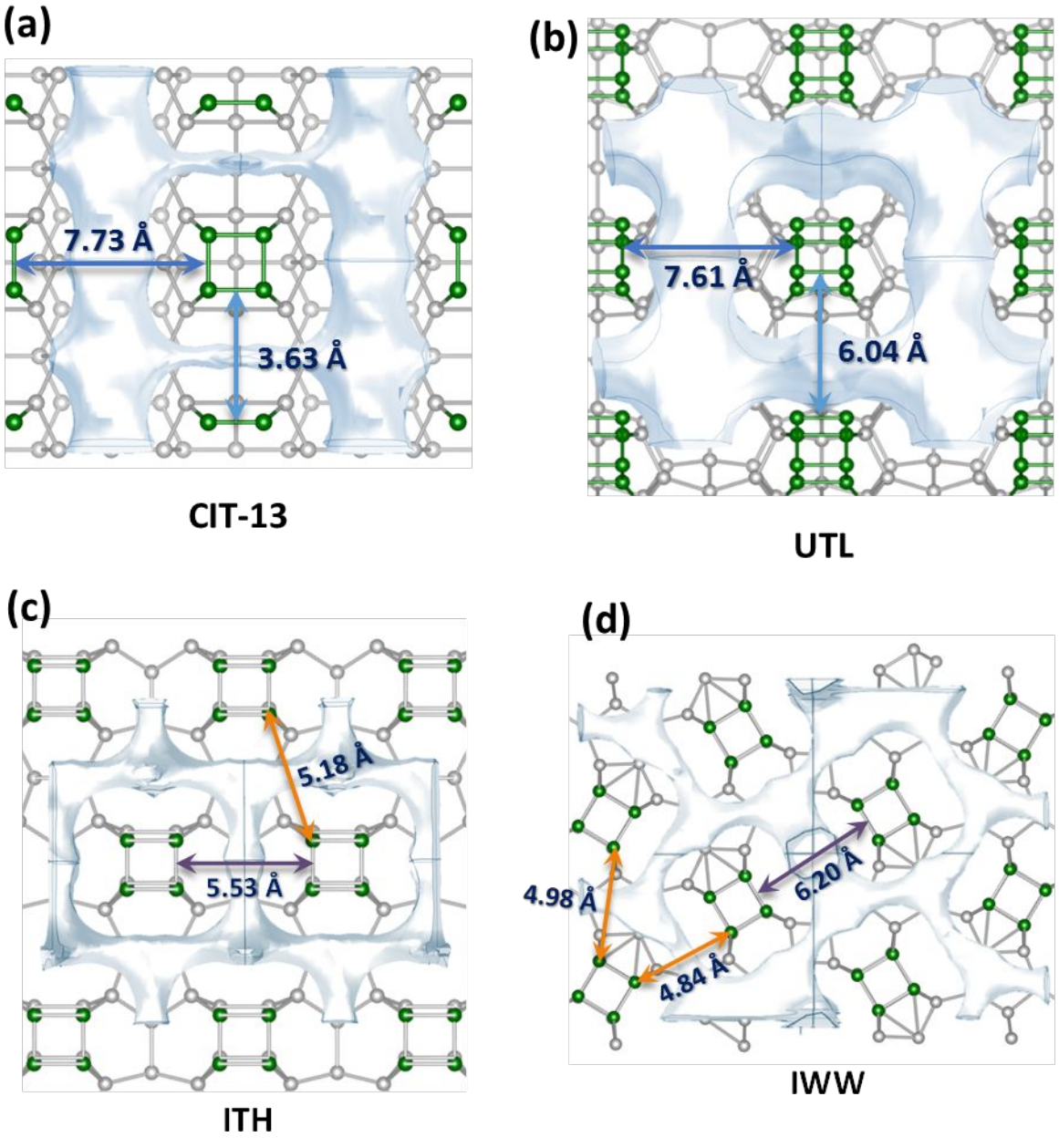


Figure S12. Visualizations of spatial arrangements of d4r units within the interlayer regions of the four selected germanosilicate frameworks: (a) CIT-13 (*CTH), (b) UTL, (c) ITH, and (d) IWW.

ADOR-type Transformation of Ge-CIT-5

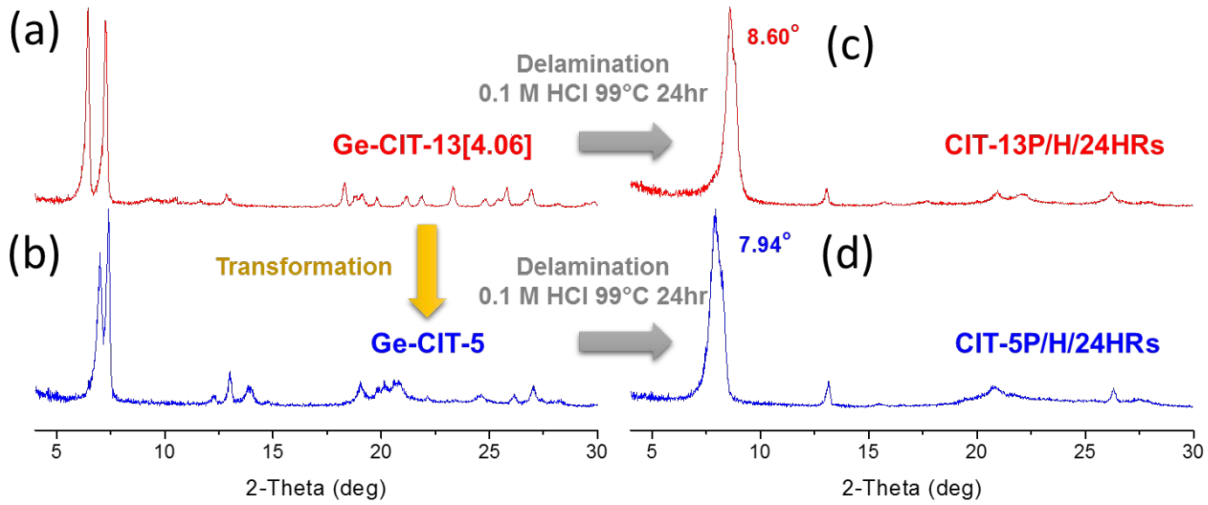


Figure S13. PXRD patterns of (a) parent Ge-CIT-13[4.06], (b) Ge-CIT-5 from Ge-CIT-13[4.06], (c) CIT-13P delaminated from the parent Ge-CIT-13[4.06], and (d) CIT-5P delaminated from Ge-CIT-5 shown in (b).

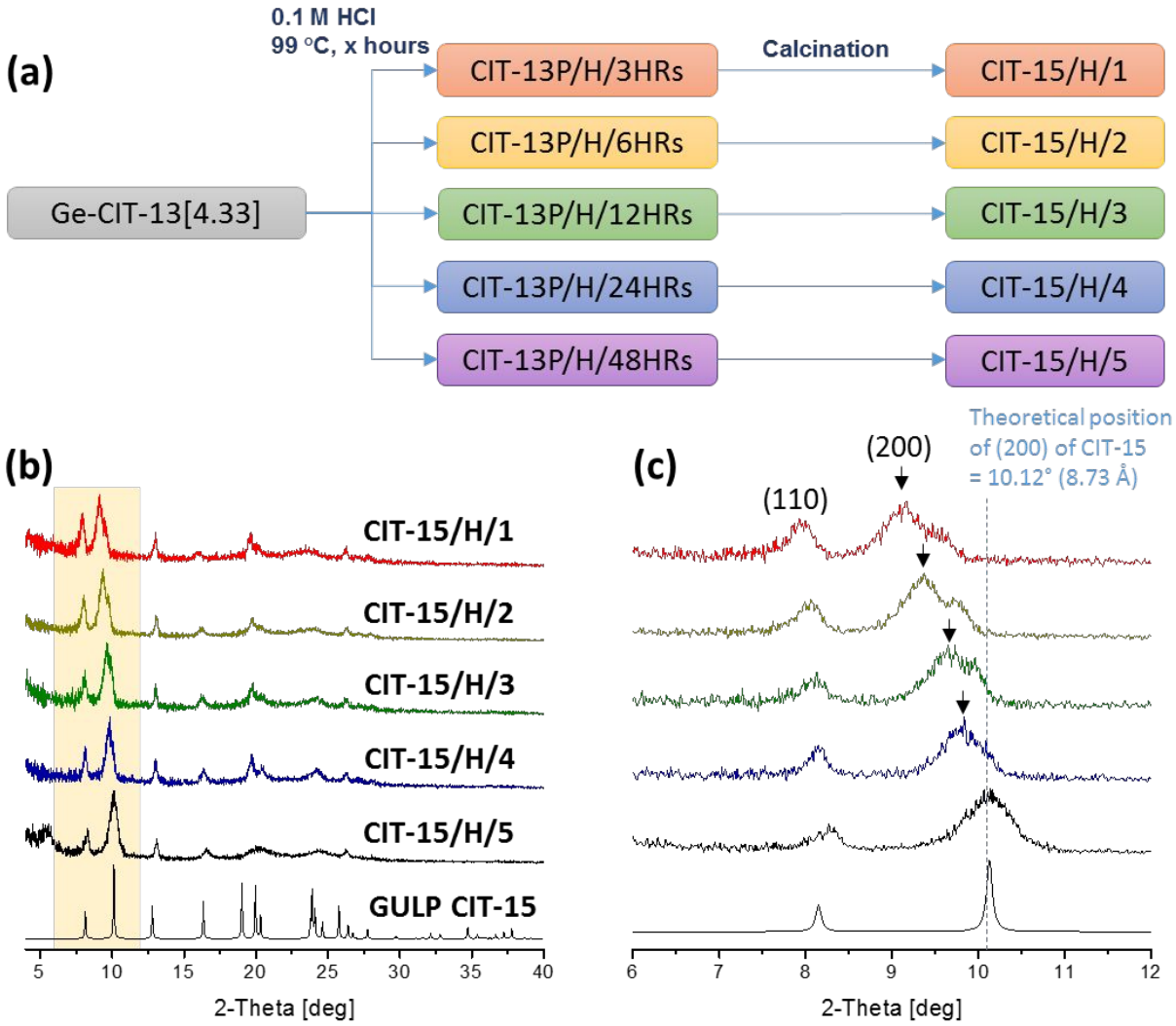


Figure S14. (a) Design of experiments, and PXRD patterns of CIT-15/H/1–5 and the theoretical PXRD pattern of CIT-15 optimized on the basis of the GULP algorithm, in the ranges of (b) 4–40° and (c) 6–12°.

Calcined Ge-CIT-13[4.33] was dispersed in 0.1 M HCl with a solid : liquid ratio of 1 g : 100 ml in a round-bottom flask and heated up to 99 °C. Fifths of the batches were taken out after 3, 6, 12, 24, and 48 hours (denoted CIT-13P/H/3, 6, 12, 24, 48HRs, respectively) and washed with distilled water and dried in vacuum at room temperature. These delaminated CIT-13P/H samples were condensed by calcining at 580 °C for 6 hours. The resultant materials were named CIT-15/H/1, 2, 3, 4, and 5, respectively. CIT-15/H/5 matched the theoretical pattern of CIT-15, but the crystallinity was poor.

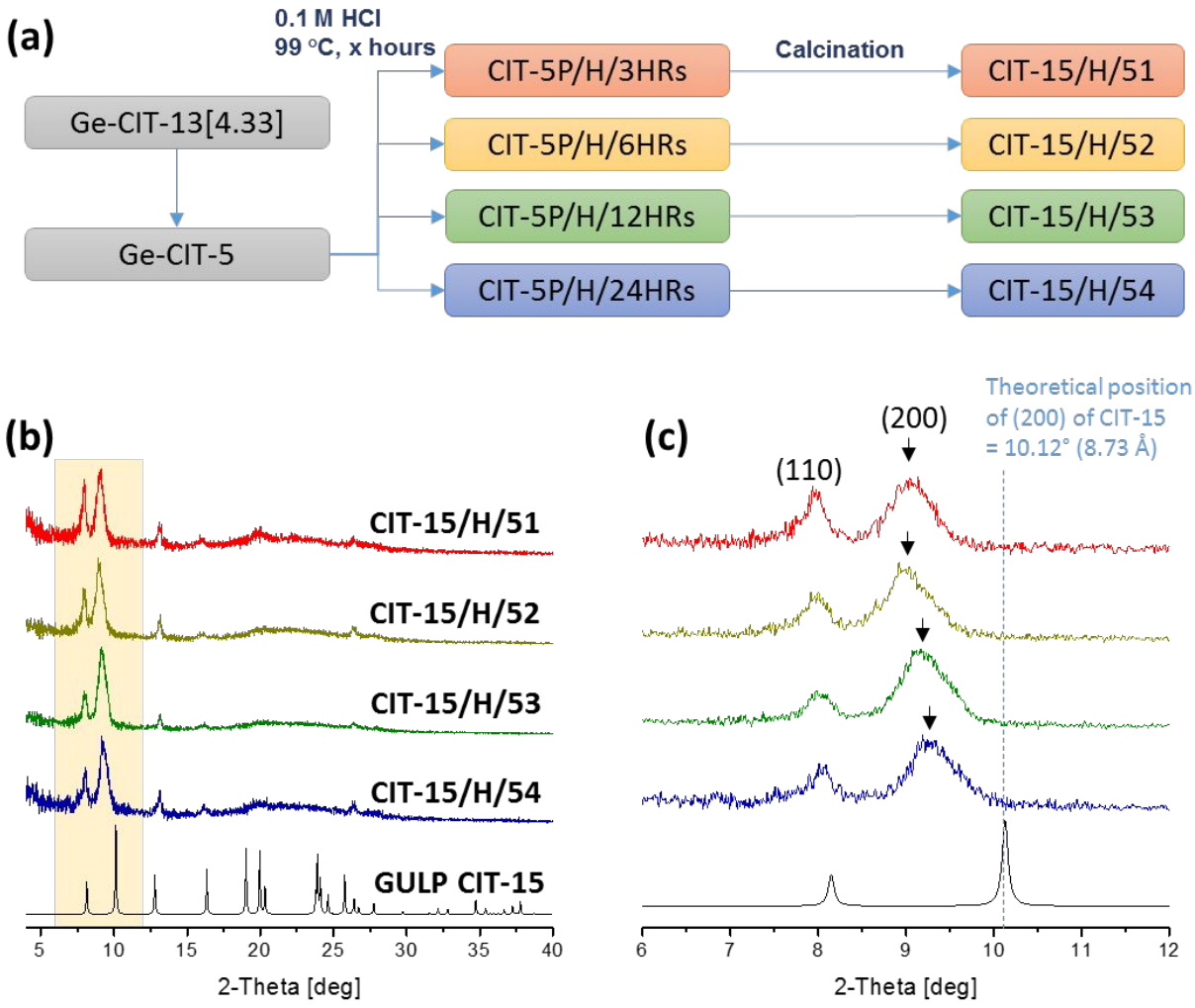


Figure S15. (a) Design of experiments, and PXRD patterns of CIT-15/H/51–54 and the theoretical PXRD pattern of CIT-15 optimized on the basis of GULP algorithm, in the ranges of (b) 4–40° and (c) 6–12°.

Calcined Ge-CIT-13[4.33] was left under an ambient lab condition (30 % relative humidity at 25 °C) for 92 days. The completion of the *CTH-to-CFI transformation was confirmed on the basis of PXRD. The resultant Ge-CIT-5 having the same Si/Ge ratio 4.33 was dispersed in 0.1 M HCl with a solid : liquid ratio of 1 g : 100 ml in a round-bottom flask and heated up to 99 °C. Fifths of the batches were taken out after 3, 6, 12, and 24 hours (denoted CIT-5P/H/3, 6, 12, 24HRs, respectively) and washed with distilled water and dried in vacuum at room temperature. These delaminated CIT-13P/H samples were condensed by calcining at 580 °C for 6 hours. The resultant materials were named CIT-15/H/51, 52,

53, and 54, respectively. None of these samples matched the theoretical pattern of CIT-15.

Postsynthetic Alumination to Al-CIT-5

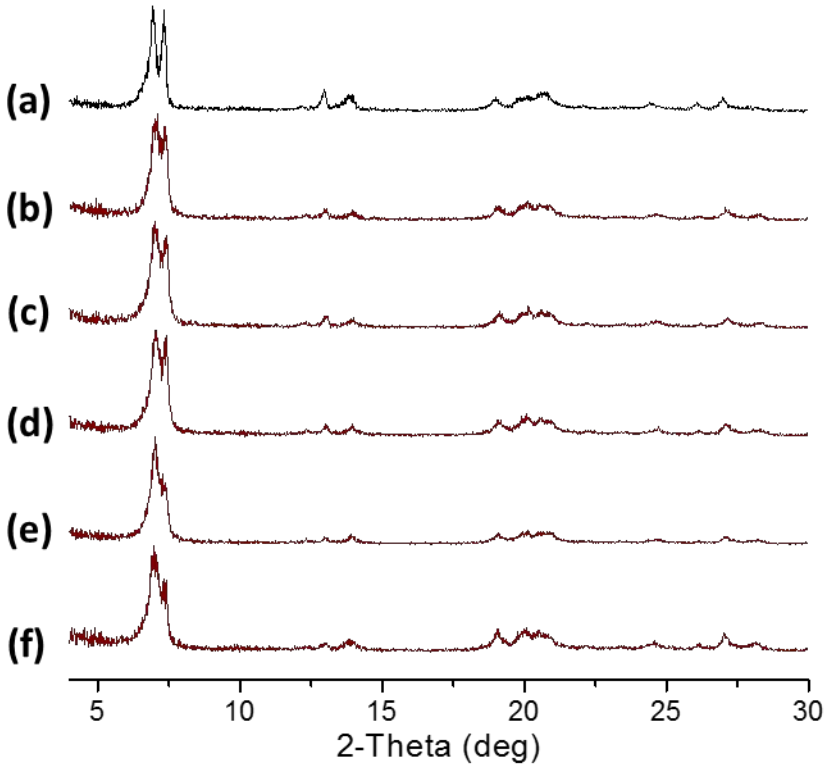


Figure S16. PXRD profiles of (a) the parent Ge-CIT-5[4.18], (b) Al-CIT-5(1), (c) Al-CIT-5(2), (d) Al-CIT-5(3), (e) Al-CIT-5(4), and (f) Al-CIT-5(5).

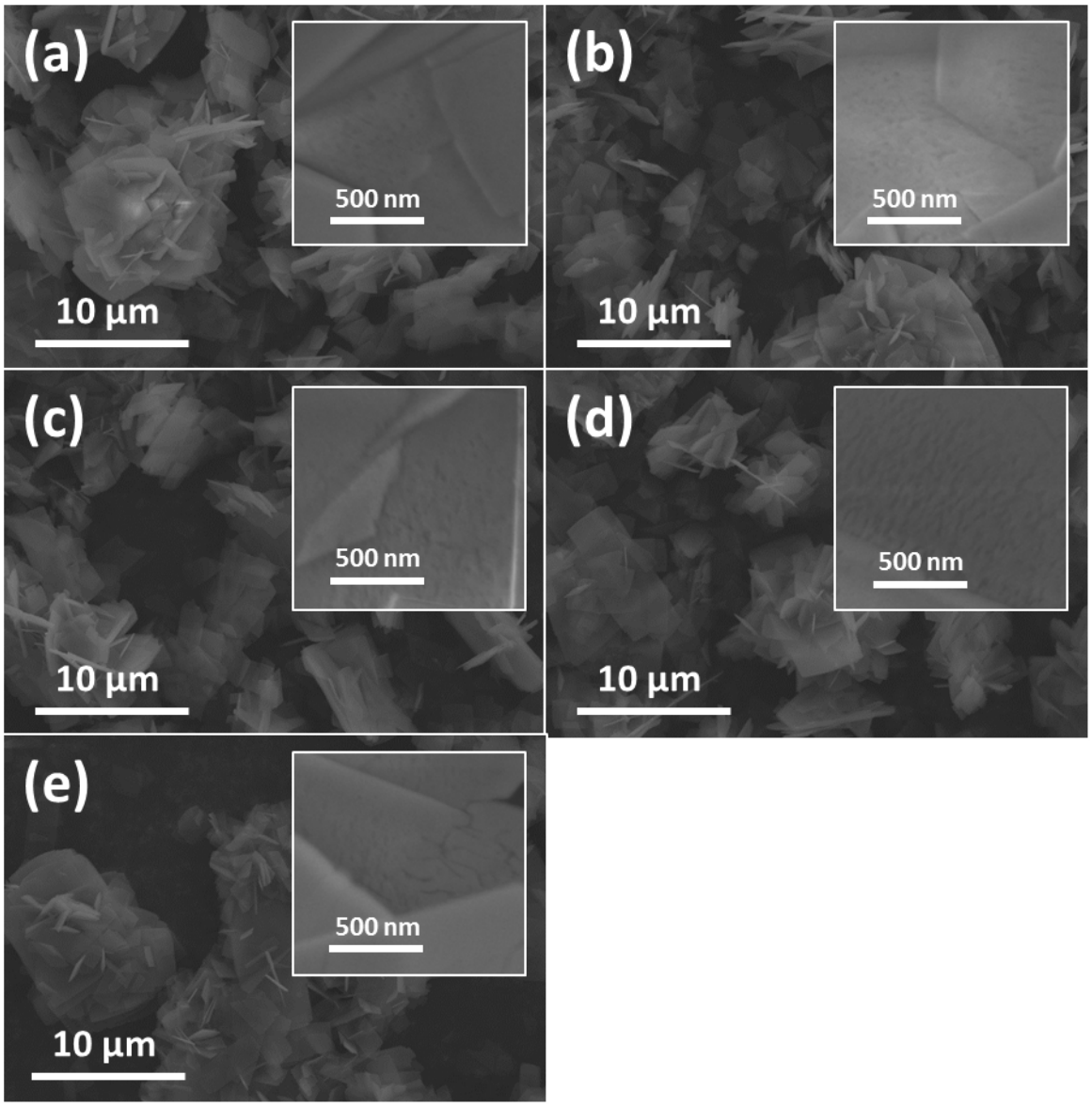


Figure S17. SEM images of (a) Al-CIT-5(1), (b) Al-CIT-5(2), (c) Al-CIT-5(3), (d) Al-CIT-5(4), and (e) Al-CIT-5(5). Insets are high resolution micrographs of macropores on crystal surfaces.

Reference

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